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[Amendments: There are no amendments made to this patent. Translator's note]

[Note: All names, addresses, companies' names, and brand names are translated in the most common manner. Japanese language does not have singular or plural words unless otherwise specified with numeral prefix or general form of plurality suffix. Translator's note]

(54) [TITLE OF THE INVENTION]

ORGANISM ATTACHMENT INHIBITOR

(57) [ABSTRACT]

[SUBJECT]

It offers an organism attachment inhibitor that shows excellent anti-polluting effect over a long period of time in water and is safe to human body as well as shows no environmental pollution.

[MEANS OF SOLUTION]

An organism attachment inhibitor in which hydrophobic material is compounded with a biodegradable resin; and it is the organism attachment inhibitor of which contact angle on the surface of said organism attachment inhibitor against water is 80° ~ 180° .

[Note: The term “organism” can be also translated as “biological” and the translator opted to use the term “biological” as stated in the Environmental Dictionary and Microbiology Dictionary. Translator’s note]

[CLAIMS]

[CLAIM ITEM 1]

It is an organism attachment inhibitor in which a hydrophobic material is compounded with a biodegradable resin, wherein the contact angle of surface of said organism attachment inhibitor against water being $80^{\circ} \sim 180^{\circ}$.

[CLAIM ITEM 2]

The organism attachment inhibitor that is described in the claim item 1, wherein said hydrophobic material is noncrystalline silica of which surface is treated to show hydrophobicity.

[CLAIM ITEM 3]

The organism attachment inhibitor that is described in the claim item 1 or 2, wherein the surface of organism attachment inhibitor is treated to be degradable with a degradable enzyme.

[DETAILED EXPLANATION OF THE INVENTION]

[0001]

[TECHNICAL FIELDS OF THIS INVENTION]

This invention relates to a in-water organism attachment inhibitor.

[0002]

[PRIOR ART]

As organism attachment inhibitors that are designed to prevent from attachment of marine organisms such as barnacles or purplish Washington clams that become attached to suction pipes that are installed in ocean or buoys that remain in constant contact with water and the like, metal compounds have been used conventionally.

[0003]

As such metal compounds, cuprous oxide, or organic tin compounds and the like are known; and in particular, organic tin compounds are widely utilized as effective organism attachment inhibitors as they show a strong microbacteriocidal effect and keep marine organisms away for long period of time.

[0004]

However, organic tin compounds show a strong toxicity; and furthermore, when they are released to sea water, degradation by microorganisms does not progress easily to tend to cause marine pollution; and as described in the "Nikkei Business issued on April 26, 1993, page 53 ~ 56", legal control over use of these is currently being emphasized.

[0005]

As organic group in-water anti-pollution agents that present no such problems as marine pollution, 3-substituted isothiazoline, or triazine derivatives and the like are disclosed in the publications of, for instance, Japanese patent applications Tokkai [Kokai] Sho 53 [1978]-12937, Tokkai Sho 54 [1979]-115386, and Tokkai Sho 46 [1971]-35934.

[0006]

These organic group in-water anti-pollution agents often remain in a powder form at regular temperature; and during their actual use, they are first dissolved in solvents such

as methyl ethyl ketone or xylene and the like, and then, resins, plasticizers, or pigments and the like are added to be used as coating materials. In addition, in order to maintain anti-polluting effect over a long period of time in water, methods of thick coating or increased compounding rate and the like have been used.

[0007]

However, thick coating presents problems including limitation placed on the physical properties of coating materials such as viscosity and the like, or workability and the like; and the method to increase compounding rate presents problems of not being able to achieve a long term anti-pollution effect although its anti-pollution effect may be improved during initial period of time. In addition, when said compounding rate is increased, problem points on environmental pollution has been pointed out from the standpoint of long term view.

[0008]

In addition, according to the publication of the Japanese patent application Tokkai Hei 4 [1992]-230201, a in-water antipollution material that shows organism attachment inhibiting effect with a single biodegradable resin, and furthermore, anti-polluting active substance is included in said biodegradable resin is disclosed. However, effect to prevent against attachment by the biodegradable resin alone remains insufficient, and when anti-polluting active substance is included, it presents problem point of environmental pollution caused by in-water release of said anti-polluting active substance.

[0009]

[SUBJECTS SOLVED BY THIS INVENTION]

Based on above-explained circumstance, purpose of this invention is to offer an organism attachment inhibitor that shows excellent anti-polluting effect in water over a long period of time, and is safe to human body, and causes no environmental pollution.

[0010]

[MEANS USED TO SOLVE THE SUBJECTS]

The organism attachment inhibitor that is characterized by the fact a hydrophobic material is compounded with a biodegradable resin, and it is constituted so that the contact angle of the surface of said organism attachment inhibitor against water being $80^{\circ} \sim 180^{\circ}$.

[0011]

The contact angle of this invention's organism attachment inhibitor against water is limited to $80^{\circ} \sim 180^{\circ}$. When said contact angle happens to be under 80°C , sufficient

hydrophobicity cannot be provided to result in insufficient anti-polluting effect; and beyond 180° cannot be realized based on the principle. Furthermore, as illustrated in the Figure 1, regarding above-explained contact angle, when a liquid body comes in contact on a solid surface, it forms a spherical-shape droplet, and the angle θ at the contact portion of this time is referred to as contact angle. According to this invention, water is used as said liquid body to measure the contact angle with the surface of organism attachment inhibitor.

[0012]

Regarding biodegradable resins that are used in this invention, no particular restrictions are placed, and for instance, the biodegradable resins that have been used conventionally including aliphatic polyesters such as polycaprolactone, polylactate, polyhydroxy butylate, polyhydroxy valerate, polybutylene succinate adipate and the like; polyamides such as polyglutamate, or polycaprolactam and the like; and copolymers of these may be used. These biodegradable resins may be used either alone or as more than two types jointly.

[0013]

Regarding said hydrophobic materials, no particular restrictions are placed, and for instance, the ones on which surfaces of various inorganic particles shown below are coated with silicone, silane, or paraffin and the like, or the ones that are treated with appropriate treatment agent to provide hydrophobicity to the substance itself may be used. As above-explained particles, for instance, silica, alumina, magnesia, or fluorine group compounds and the like may be mentioned.

[0014]

As hydrophobic material, noncrystalline silica that is surface treated to show hydrophobicity is particularly favorable.

[0015]

Regarding above-explained noncrystalline silica, it is generally referred to as moist silicon, wet silica, or synthetic silicate and like; and it is constituted of Si-O mesh structure, and is either noncrystalline or amorphous silica that does not have set crystal structure. According to this invention, any of synthetic noncrystalline silica that is manufactured through, for instance, a flame hydrolysis method (aerosol method), a dry-type method, an Aerogel method, or a wet method and the like, or natural noncrystalline silica may be used. In addition, although primary particles are aggregated to become secondary particles in some cases, they may be also used in this invention.

[0016]

Regarding the method to treat surface of above-explained noncrystalline silica to hydrophobic, for instance, surface treatment methods such as coating by wax, or

chemical reaction of appropriate silane and OH group on the surface of noncrystalline silica and the like may be used to provide alkyl chain on the surface; and it is possible to convert OH group on the surface from hydrophilic to hydrophobic through such methods, and treatment methods are not particularly restricted. Many of generally commercialized hydrophobic noncrystalline silica show their surfaces being converted to hydrophobic through chemical reaction with silicon oil, silane, or methyl silyl and the like; and these may be also used.

[0017]

Compounding rate of above-explained hydrophobic material is 1 ~ 90 parts by weight, or more preferably, 20 ~ 60 parts by weight based on 100 parts by weight of biodegradable resin. When hydrophobic material happens to be under 1 part by weight, effect of hydrophobicity remains poor, and when it happens to exceed 90 parts by weight, it does not get combined with said biodegradable resin, and becomes difficult to obtain organism attachment inhibitor as one piece [body].

[0018]

Surface of above-explained organism attachment inhibitor may be treated to be degradable with a degradable enzyme. The degradable enzyme that can be used at this time shows no particular restrictions as long as it is the enzyme that can degrade this invention's biodegradable resin, and for instance, enzymes that degrade ester bonding such as lipase, esterase, or amylase and the like may be used. Regarding the method to allow said degradable enzyme to work, a method that directly works degradable enzyme, or a method that allows contact microorganism capable of secreting degradable enzyme outside of the cell or on cell surface with above-explained inhibitor may be mentioned.

[0019]

Through surface treatment of above-explained organism attachment inhibitor by working degradable enzyme or degradable microorganism, hydrophobic material may be exposed to the surface of inhibitor to display performance of attachment prevention from the initial period, and it is more favorable.

[0020]

[ACTIONS]

According to this invention's organism attachment inhibitor, through converting resin surface to hydrophobic by exposing hydrophobic material on the surface of biodegradable resin, it prevents from attachment of organism such as barnacles, sea squirts, or algae and the like in water. In addition, when said resin surface becomes polluted by microorganism in sea water, hydrophobicity becomes lost, and although gradual organism attachment may occur, new resin surface is formed through degradation of biodegradable resin to again expose hydrophobic material to create a state where organisms are difficult to attach again to show an excellent pollution prevention effect over long period of time.

[0021]

[IMPLEMENTATION FORMATS OF THIS INVENTION]

Examples are described below to further explain this invention in details; however, this invention should not be limited to these examples only.

[0022]

(EXAMPLE 1)

As a biodegradable resin, polycaprolactone (brand name :Pulakucell H7 [transliteration] made by Dicell Kagaku Kogyo K.K.) 100 parts by weight was fused in a 180°C plastomill to form hydrophobic noncrystalline silica; and 20 parts by weight of silica that was surface treated with dimethyl silicone oil (brand name: Aerosil RY200S [transliteration] made by Nihon Aerosil K.K.) was added, and this was kneaded for 5 minutes at 60 rpm, and then, a hot press molding machine was used to give organism attachment inhibitor showing 3 mm thickness. Thus given organism attachment inhibitor was punched out to 5 cm x 5 cm to be used as specimens.

[0023]

(EXAMPLE 2)

Specimens were prepared in the same manner as explained in the example 1 by using aliphatic polyester (brand name: Pionole #3010 [transliteration] made by Showa Denko K.K.) as a biodegradable resin.

[0024]

(EXAMPLE 3)

Specimens were prepared in the same manner as explained in the example 1 by using aliphatic polyester (brand name: Pionole #1030 made by Showa Denko K.K.) as a biodegradable resin.

[0025]

(EXAMPLE 4)

Specimens were prepared in the same manner as explained in the example 1 by using silica that is surface treated with trimethyl silyl group (brand name: Aerosil R812 made by Nihon Aerosil K.K.) as a hydrophobic noncrystalline silica.

[0026]

(EXAMPLE 5)

Specimens were prepared in the same manner as explained in the example 1 by changing the compounding ratio of hydrophobic noncrystalline silica of the example 1 to 50 parts by weight.

[0027]

(EXAMPLE 6)

An enzyme solution was prepared by diluting enzyme: *R. arrhizus* lipase (made by SIGMA K.K.) with a buffer solution (KH_2PO_4 , PH7); and it was added to the solution in which 1 g of surfactant (Polysurf made by Daiichi Kogyo Seiyaku K.K.) to 100 ml of pure water; and specimen given by the example 1 were immersed for 20 hours in this solution to be treated with enzyme to give specimens.

[0028]

(EXAMPLE 7)

The specimens given by the example 2 were treated with enzyme in the same manner as explained in the example 6 to give other specimens.

[0029]

(EXAMPLE 8)

The specimens given by the example 3 were treated with enzyme in the same manner as explained in the example 6 to give other specimens.

[0030]

(EXAMPLE 9)

The specimens given by the example 5 were treated with enzyme in the same manner as explained in the example 6 to give other specimens.

[0031]

(COMPRATIVE EXAMPLE 1)

Acryl resin sheet with 3 mm thickness (brand name: Acrylite EX [transliteration] made by Mitsubishi Rayon K.K.) was cut to 5 cm x 5 cm to be used as specimens.

[0032]

(COMPRATIVE EXAMPLE 2)

Polycaprolactone (brand name: Pulakucell H7 [transliteration] made by Dicell Kagaku Kogyo K.K.) that is a biodegradable resin was formed in a sheet form with 3 mm thickness along by using a hot press molding machine. Thus given sheet was punched out to 5 cm x 5 cm to be used as specimens.

[0033]

(COMPARATIVE EXAMPLE 3)

Aliphatic polyester (brand name: Pionole #3010 [transliteration] made by Showa Denko K.K.) that is a biodegradable resin used in the example 2 was formed as a sheet with 3 mm thickness along by using a hot press molding machine. Thus given sheet was punched out to 5 cm x 5 cm to be used as specimens.

[0034]

(COMPARATIVE EXAMPLE 4)

The specimen were prepared in the same manner as explained in the example 1 by using hydrophilic silica (brand name: Aerosil 200 made by Nihon Aerosil K.K.) as a noncrystalline silica.

[0035]

Anti-polluting test that evaluates attachment of marine organisms was implemented in the manner explained below. 100 vertical striped barnacles were placed in a beaker containing 200 ml of filtered sea water; and specimen of each example and each comparative example were immersed, and were left stationary in a dark place at 23°C. They were taken out after 72 hours to study the number of vertical striped barnacles that were attached and metamorphosed to the specimen to judge attachment inhibition effect. The test was repeated for 3 times to seek attachment rate (number of attachments % of 100 barnacles), and its mean value is shown in the Table.

[0036]

In addition, surface contact angle was measured by using contact angle gauge (CA-X 150 model made by Kyowa Kaimen Kagaku K.K.) that is of 3 points measuring image treatment type. Effect of attachment inhibition and results of surface contact angle are shown in the Table 1.

[0037]

[Table 1]

	Attachment rate of barnacles (%)	Surface contact angle (°)
Example 1	8	85
Example 2	5	90
Example 3	6	95
Example 4	8	87
Example 5	5	110
Example 6	3	125
Example 7	2	130
Example 8	3	128
Example 9	1	158
Comparative example 1	75	60
Comparative example 2	60	70
Comparative example 3	50	50
Comparative example 4	83	25

[0038]

[EFFECTS OF THIS INVENTION]

According to this invention's organism attachment inhibitor, by converting the surface of biodegradable resin to hydrophobic and further carrying out an enzyme treatment, the contact angle against water becomes superbly large; and this prevents from attachment of organism and anti-polluting effect is enhanced from the stage of initial period. In addition, with gradual degradation of biodegradable resin in sea water, it degrades in sea water with even a slight attachment of organism to enable to retain always a new hydrophobic surface over a long period of time to maintain anti-polluting effect. In addition, as no toxic substance is used, it is safe to human body and it can provide anti-polluting effect with no environmental pollution.

[0039]

[BRIEF DESCRIPTION OF THE FIGURES]

[FIGURE 1]

It illustrates a schematic view that shows contact angle.

[DESCRIPTION OF CODES]

θ : contact angle

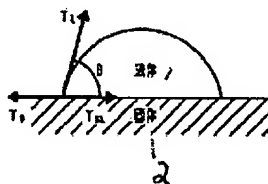
γ_s : surface tension of solid

γ_l : surface tension of liquid body

γ_{sl} : interfacial tension of solid and liquid body

[Figure 1]

1; liquid body, 2: solid



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(54) 【発明の名称】 生物付着防止材

(57) 【要約】

【課題】 水中で長期間防汚効果に優れ、人体に対して安全でかつ環境汚染のない生物付着防止材を提供する。

【解決手段】 生分解性樹脂に疎水性材料が配合された生物付着防止材であって、該生物付着防止材表面の水に対する接触角が80°～180°である生物付着防止材。

【特許請求の範囲】

【請求項1】 生分解性樹脂に疎水性材料が配合された生物付着防止材であって、該生物付着防止材表面の水に対する接触角が $80^{\circ} \sim 180^{\circ}$ であることを特徴とする生物付着防止材。

【請求項2】 前記疎水性材料が疎水性に表面処理された非晶質シリカであることを特徴とする請求項1記載の生物付着防止材。

【請求項3】 生物付着防止材の表面が分解酵素によって分解処理されていることを特徴とする請求項1又は請求項2記載の生物付着防止材。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、水中生物付着防止材に関する。

【0002】

【従来の技術】従来より、海中に設置される吸水管、海水に絶えず接するブイ等にフジツボ、ムラサキガイ等の海洋生物が付着することを防止するための生物付着防止材として金属化合物が用いられてきた。

【0003】このような金属化合物としては、亜酸化銅、有機すず化合物等が知られており、特に有機すず化合物は、強い殺菌力を有しており、長期間にわたって海洋生物を寄せ付けないので、有効な生物付着防止材として広く利用されている。

【0004】しかし、有機すず化合物は毒性が強く、また海水中に放出された場合、微生物による分解が容易に進まず海洋汚染を引き起こし易いので、「日経ビジネス、1993年4月26日号、P. 53～56」に記載されているように、現在ではその使用に対する法的規制が強まりつつある。

【0005】このような海洋汚染の問題がない有機系水中防汚剤として、例えば、特開昭53-12937号公報、特開昭54-115386号公報、特開昭46-35934号公報には、3-置換イソチアゾリン、トリアジン誘導体等が、開示されている。

【0006】これら有機系水中防汚剤は、常温で粉体であるものが多く、実際に使用するときにはメチルエチルケトン、キシレン等の溶剤に溶かした後、樹脂、可塑剤、顔料等を加え塗料として用いられる。また、水中での防汚効果を長期間持続するために、厚塗りや、配合量増加等の方法が採られている。

【0007】しかし、厚塗りは、粘度等の塗料物性の限界や作業性等に問題があり、配合量を増加する方法は、防汚剤が単位時間当たり水中で溶出する量が増えるので、初期の防汚効果は向上するものの、長期の防汚効果は得られない等の問題があった。また、配合量を増加する場合、長期的に見て、環境を汚染するという問題点があった。

【0008】また、特開平4-230201号公報に

は、生分解性樹脂単独で生物付着防止効果を有し、さらに生分解性樹脂に防汚活性物質を含有させた水中防汚材料が開示されている。しかしながら、生分解性樹脂単独では付着防止効果が不十分であり、防汚活性物質を含有させた場合、前記防汚活性物質の水中放出による環境汚染の問題点がある。

【0009】

【発明が解決しようとする課題】本発明は、上記に鑑み、水中で長期間防汚効果に優れ、人体に対して安全でかつ環境汚染のない生物付着防止材を提供することを目的とする。

【0010】

【課題を解決するための手段】生分解性樹脂に疎水性材料が配合された生物付着防止材であって、該生物付着防止材表面の水に対する接触角が $80^{\circ} \sim 180^{\circ}$ であることを特徴とする生物付着防止材を構成することに存する。

【0011】本発明の、生物付着防止材の水に対する接触角は $80^{\circ} \sim 180^{\circ}$ に制限される。接触角が 80° 未満では十分な疎水性が付与されないため、防汚効果が不十分となり、 180° 以上は原理上ありえない。尚、上記接触角は、図1に示すように、固体表面上に液体が触れると、球状の液滴を生じるが、このときの接触部分の角度 θ を接触角と呼ぶ。本発明では液体として水を用い、生物付着防止材表面の接触角を測定した。

【0012】本発明で使用される生分解性樹脂としては特に限定されるものではなく、例えば、ポリカプロラクトン、ポリ乳酸、ポリヒドロキシブチレート、ポリヒドロキシバリレート、ポリブチレンスクシネートアジベート等の脂肪族ポリエステル；ポリグルタミン酸、ポリカプロラクタム等のポリアミド；及びこれらの樹脂の共重合体等の従来より公知の生分解性樹脂を用いることができる。これらの生分解性樹脂は単独で用いられてもよく2種類以上が併用されてもよい。

【0013】前記疎水性材料としては特に限定されるものではなく、例えば、下記に示す種々の無機粒子の表面をシリコーン、シラン、パラフィン等でコーティングしたり、適当な処理剤で加工して物質自身に疎水性を持たせたものを用いることができる。上記の粒子としては、例えば、シリカ、アルミナ、マグネシア、フッ素系化合物等が挙げられる。

【0014】疎水性材料として、特に疎水性に表面処理された非晶質シリカが好ましい。

【0015】上記非晶質シリカは、一般に含水珪素、湿式シリカ、合成珪酸等と呼ばれ、 Si-O の網目構造から成り、一定の結晶構造を持たない非晶質または無定形のシリカである。本発明では、例えば火炎加水分解法（アエロジル法）、乾式法、エアロゲル法、湿式法等で製造される合成非晶質シリカ、または天然非晶質シリカなら何れでも良い。また、1次粒子が凝集して2次粒子

となっていることもあるが、これらも本発明で使用できる。

【0016】上記の非晶質シリカの表面を疎水性に処理する方法としては、例えばワックスによるコーティングや適当なシランと非晶質シリカの表面OH基との化学反応等の表面処理法によって表面にアルキル鎖を持たせたものであり、このような方法により、表面のOH基が親水性であるのを疎水性にすることができ、特に処理方法は限定されない。一般に市販されている疎水性非晶質シリカの多くは該表面をシリコンオイル、シラン、メチルシリル基等との化学反応によって疎水性にしており、これらを使用しても良い。

【0017】上記疎水性材料の配合量は生分解性樹脂100重量部に対して、1～90重量部、好ましくは20～60重量部である。疎水性材料が1重量部未満では疎水性の効果が乏しく、90重量部を超えると該生分解性樹脂とまとまらず一体的な生物付着防止材とすることが難しくなるからである。

【0018】上記生物付着防止材の表面は分解酵素により分解処理が施されてもよい。ここで用いられる分解酵素としては、本発明の生分解性樹脂を分解できる酵素であれば特に制限はなく、例えば、リパーゼ、エステラーゼ、アミラーゼのようなエステル結合を分解する酵素が使用される。分解酵素を作用させる方法としては、分解酵素を直接作用させる方法、または、分解酵素を菌体外或いは菌体表面に分泌可能な微生物を上記防止材に接触させる方法が用いられる。

【0019】上記生物付着防止材を分解酵素や分解微生物を作用させ、表面処理することにより、防止材表面に疎水性材料を露出させて、初期から付着防止の性能を発揮させることができ、より好ましい。

【0020】

【作用】本発明の、生物付着防止材は、生分解性樹脂の表面に疎水性材料を露出させて、前記樹脂表面を疎水化する事により、水中のフジツボ、ホヤ、藻類等の生物が付着するのを防止する。また、前記樹脂表面が海水中の微生物等により汚染されてくると、疎水性が損なわれ、徐々に生物付着が起こるが、生分解性樹脂の分解により、新しい樹脂表面ができ、再び疎水性材料が露出する事により、生物が付着しにくい状態が再びできあがり、長期間防汚効果に優れたものとなる。

【0021】

【発明の実施の形態】以下に実施例を掲げて本発明を更に詳しく説明するが、本発明はこれら実施例のみに限定されるものではない。

【0022】（実施例1）生分解性樹脂として、ポリカプロラクトン（ダイセル化学工業社製、商品名：ブラクセルH7）100重量部を180℃のプラストミル中で溶融し、疎水性非晶質シリカとして、ジメチルシリコンオイルで表面処理したシリカ（日本アエロジル社

製、商品名：アエロジルRY200S）を20重量部加え、毎分60回転の速度で5分間混練し、その後、熱プレス成形機を用いて厚さ3mmの生物付着防止材を得た。得られた生物付着防止材を5cm×5cmに打ち抜き、試料とした。

【0023】（実施例2）生分解性樹脂として、脂肪族ポリエステル（昭和電工社製、商品名：ビオノーレ#3010）を使用した以外は、実施例1と同様にして試料を得た。

【0024】（実施例3）生分解性樹脂として、脂肪族ポリエステル（昭和電工社製、商品名：ビオノーレ#1030）を使用した以外は、実施例1と同様にして試料を得た。

【0025】（実施例4）疎水性非晶質シリカとしてトリメチルシリル基で表面処理したシリカ（日本アエロジル社製、商品名：アエロジルR812）を使用した以外は、実施例2と同様にして試料を得た。

【0026】（実施例5）実施例1の疎水性非晶質シリカの配合割合を50重量部に変更した以外は実施例1と同様にして試料を得た。

【0027】（実施例6）酵素：R. arrhizus lipase（SIGMA社製）を緩衝溶液（KH₂PO₄，PH7）で希釈した酵素溶液を作り、界面活性剤（Plysurf，第一工業製薬社製）1gを純水100mlに溶かした溶液に加え、実施例1で得られた試料をこの溶液中に20時間浸漬し、酵素処理したものを試料とした。

【0028】（実施例7）実施例2で得られた試料を実施例6と同様に酵素処理して試料を得た。

【0029】（実施例8）実施例3で得られた試料を実施例6と同様に酵素処理して試料を得た。

【0030】（実施例9）実施例5で得られた試料を実施例6と同様に酵素処理して試料を得た。

【0031】（比較例1）厚さ3mmのアクリル樹脂板（三菱レーヨン社製、商品名：アクリライトEX）を5cm×5cmに切断したものを試料とした。

【0032】（比較例2）生分解性樹脂であるポリカプロラクトン（ダイセル化学工業社製、商品名：ブラクセルH7）を単独で熱プレス成形機を用いて厚さ3mmのシート状に成形した。得られたシートを5cm×5cmに打ち抜き、試料とした。

【0033】（比較例3）実施例2で用いた生分解性樹脂である脂肪族ポリエステル（昭和電工社製、商品名：ビオノーレ#3010）を単独で熱プレス成形機を用いて厚さ3mmのシート状に成形した。得られたシートを5cm×5cmに打ち抜き、試料とした。

【0034】（比較例4）非晶質シリカとして親水性のもの（日本アエロジル社製、商品名：アエロジル200）を使用した以外は、実施例1と同様にして試料を得た。

【0035】海洋生物の付着性を評価する防汚試験は、以下のように実施した。ろ過海水200mlの入ったビーカー内にタテジマフジツボ100匹を入れ、各実施例及び各比較例の試料を浸漬し、23℃の暗所に静置した。72時間後に取り出し、試料に付着変態したタテジマフジツボの数を調べ、付着阻止効果を判定した。試験は3回繰返し付着率（100匹の内、付着した個数％）を求め、その平均値を表中に示した。

【0036】また、表面接触角は、3点測定画像処理方式の接触角計（協和界面科学社製；CA-X150型）を用いて測定した。付着阻止効果及び表面接触角の結果を表1に示す。

【0037】

【表1】

		フジツボの付着率 (%)	表面接触角 (度)
実 施 例	1	8	85
	2	5	90
	3	6	95
	4	8	87
	5	5	110
	6	3	125
	7	2	130
	8	3	128
	9	1	158
比 較 例	1	75	60
	2	60	70
	3	50	50
	4	83	25

【0038】

【発明の効果】本発明の生物付着防止材は、生分解性樹脂の表面を疎水性にし、更に酵素処理を行うことにより、水に対する接触角が格段に大きくなり、このことが生物の付着を防止しており、初期段階から防汚効果を高めている。また、長期的には、生分解性樹脂が海水中で徐々に分解する事により、わずかでも付着した生物とともに海水中に分解し、常に新しい疎水性表面を保持し、防汚効果を持続させるのである。また、毒物を使用していないので、人体に対して安全でかつ環境汚染のない防汚効果を得ることができる。

【0039】

【図面の簡単な説明】

【図1】接触角を示す概念図である。

【符号の説明】

θ : 接触角

γ_s : 固体の表面張力

γ_l : 液体の表面張力

γ_{sl} : 固体と液体の界面張力

【図1】

